

**OXIDATION OF Zr ALLOYS
IN HIGH PRESSURE STEAM
*AND SOME RESULTS UNDER
ATMOSPHERIC PRESSURE***

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- Cathcart-Pawel correlation

INTRODUCTION

- Verification of safety margins for high-burnup fuel and fuels clad with new alloys
- U.S. Regulatory Guide (RG) 1.157 § 3.2.5.1 recognizes the effect of steam pressure for intermediate break LOCA
- New publications after RG 1.157 was issued
- Follow-up of 28th WRSN paper to calculate what would have been the ECR criterion if the Cathcart-Pawel correlation would have been used in 1973
- Some words on the Cathcart and Pawel's data

INTERMEDIATE BREAK LOCAs

- USNRC LOCA PIRT, NUREG/CR-6744
(3-inches Appendix K calculation):
 - Peak Clad Temperature $\sim 1000^{\circ}\text{C}$
 - Time above $800^{\circ}\text{C} \sim 1000\text{s}$
 - Pressure $\sim 35\text{bars}$
- Some French fuel managements (delayed primary pumps trip):
 - Time above $800^{\circ}\text{C} \sim 300\text{s}$
 - Pressure above 25bars

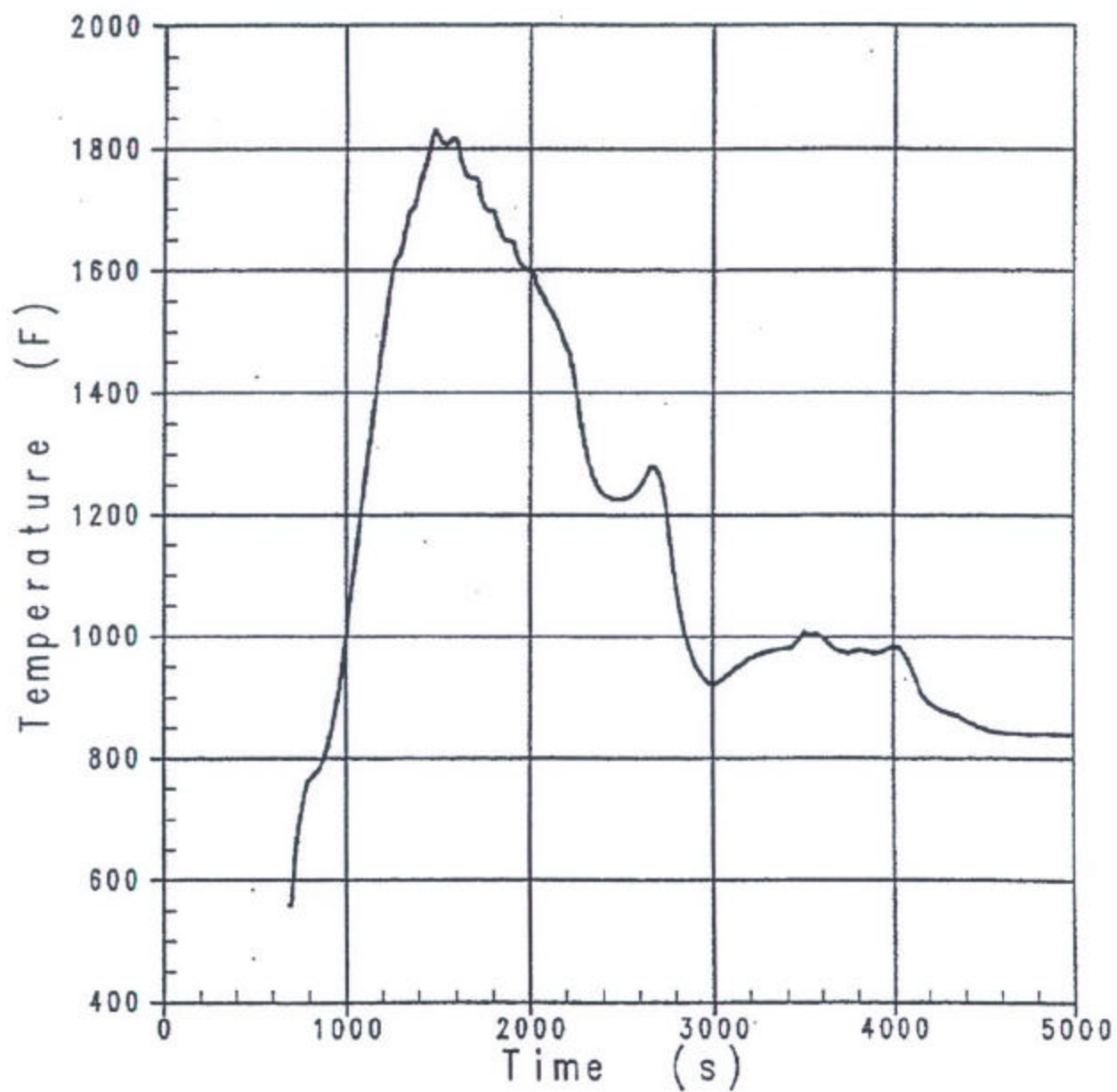


Figure 9.

3-INCH PEAK CLAD TEMPERATURE

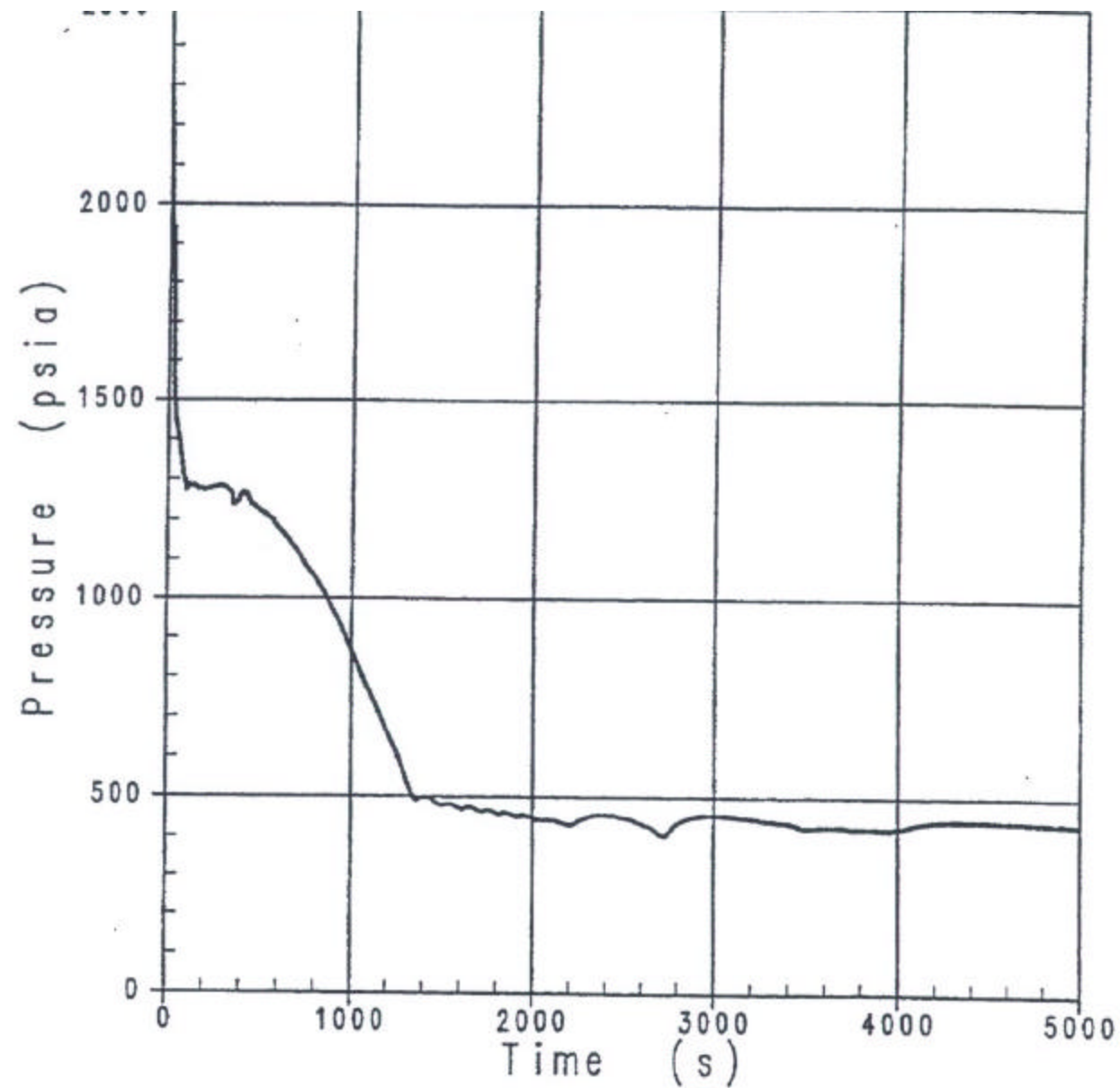
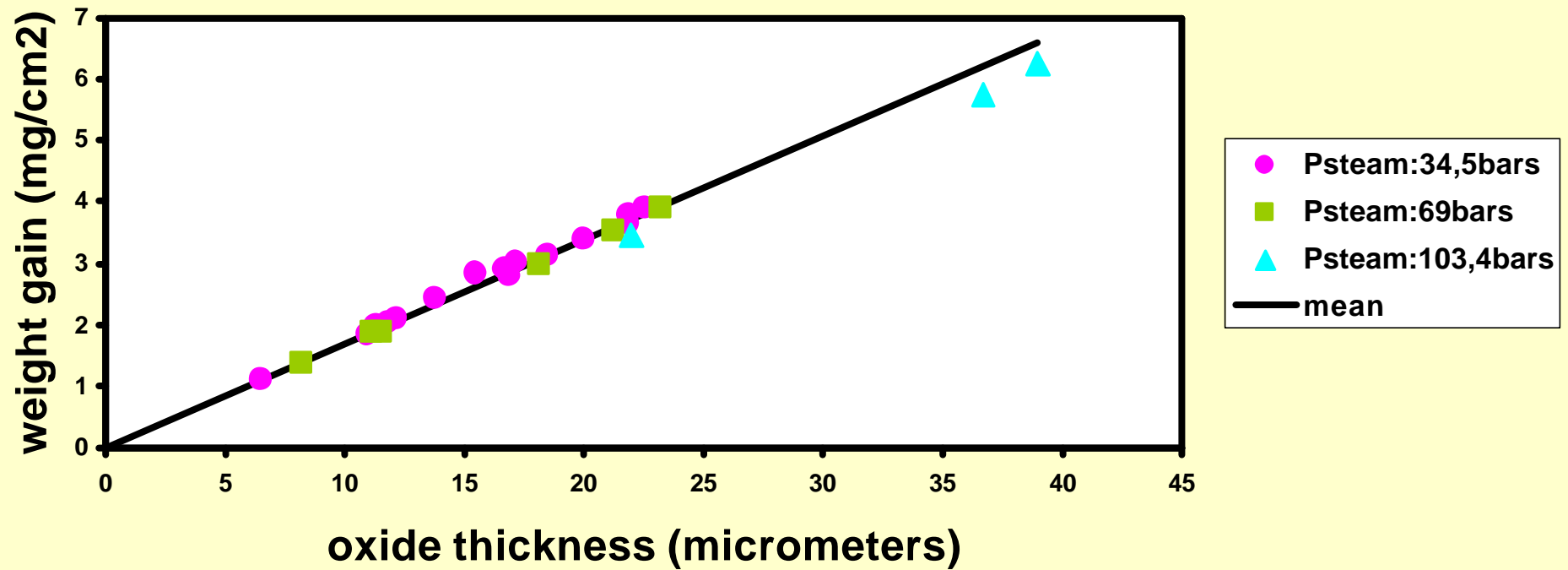


Figure 7.
3-INCH PRESSURIZER PRESSURE

ZRY-4 / HIGH PRESSURE STEAM

- Pawel et al. were alone to publish both oxide layer growth and weight gain in open literature
 - Use of Pawel's data to correlate weight gain and oxide layer growth
- Park et al. didn't publish full tabulated data in open literature
 - Use of Park's empirical model

correlation between weight gain and oxide thickness (Pawel's tests)



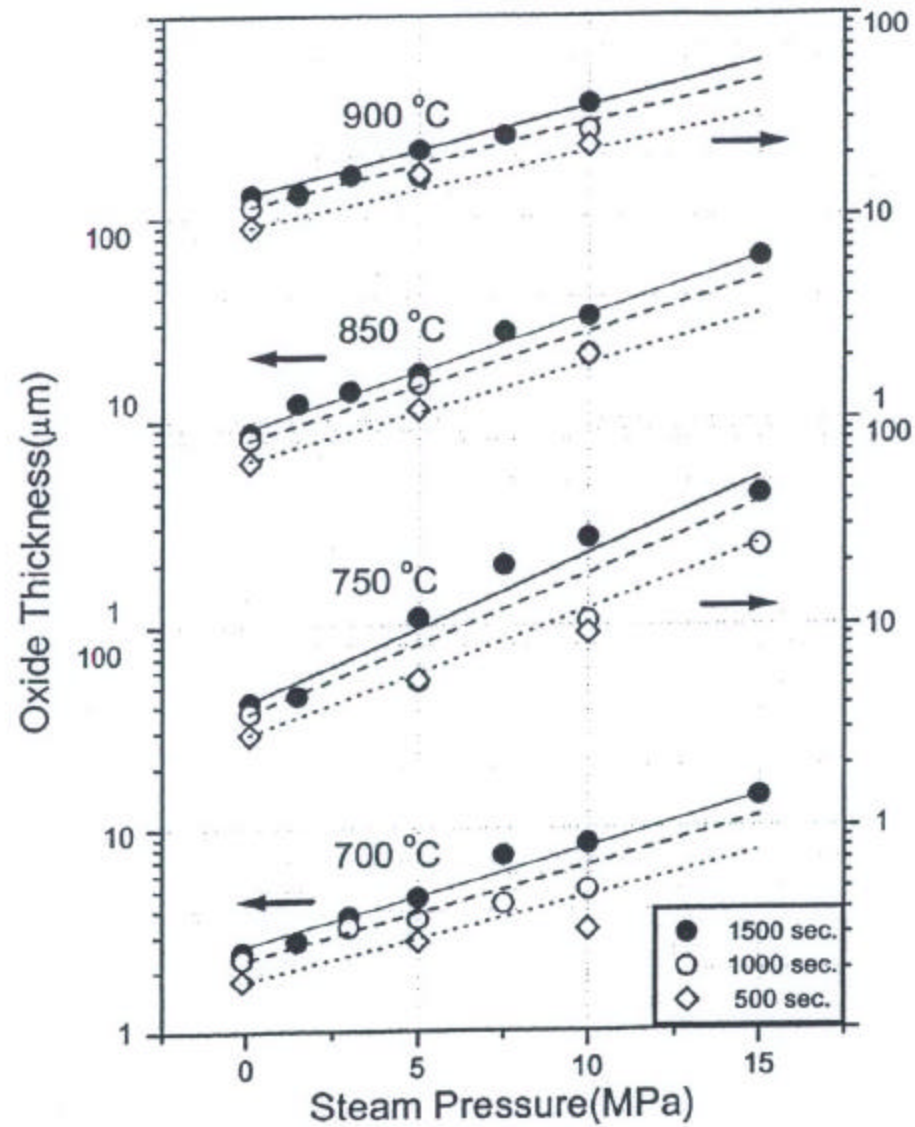
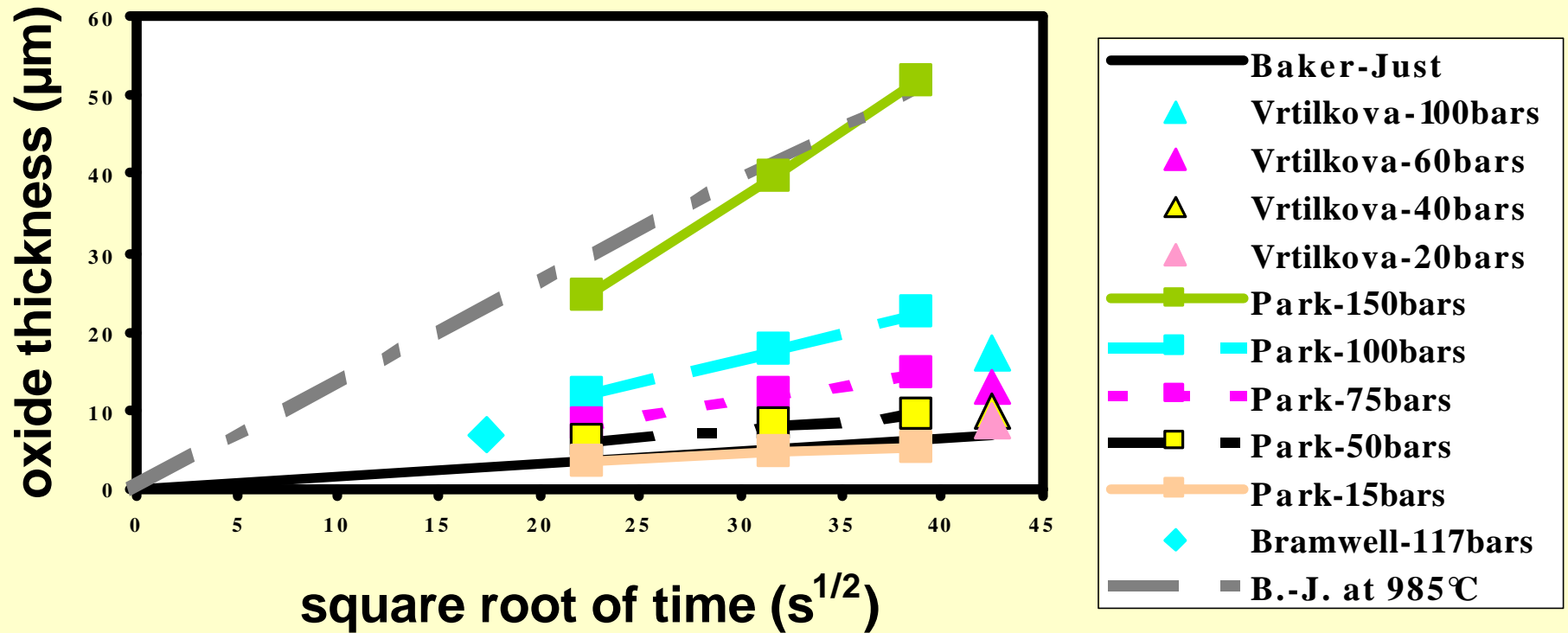
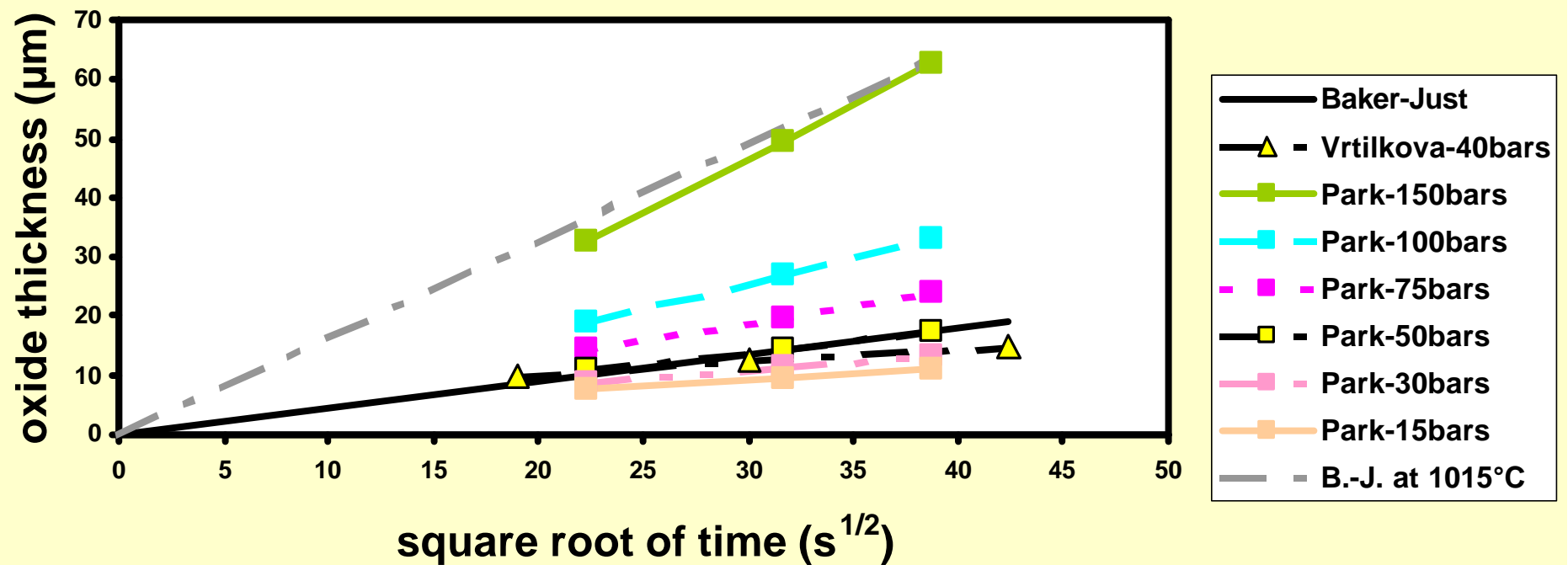


Fig.6. Comparison of suggested model to the measured data.

Zry - oxide thickness at 750°C as a function of square root of time and steam pressure



Zry - oxide thickness at 850°C as a function of square root of time and steam pressure



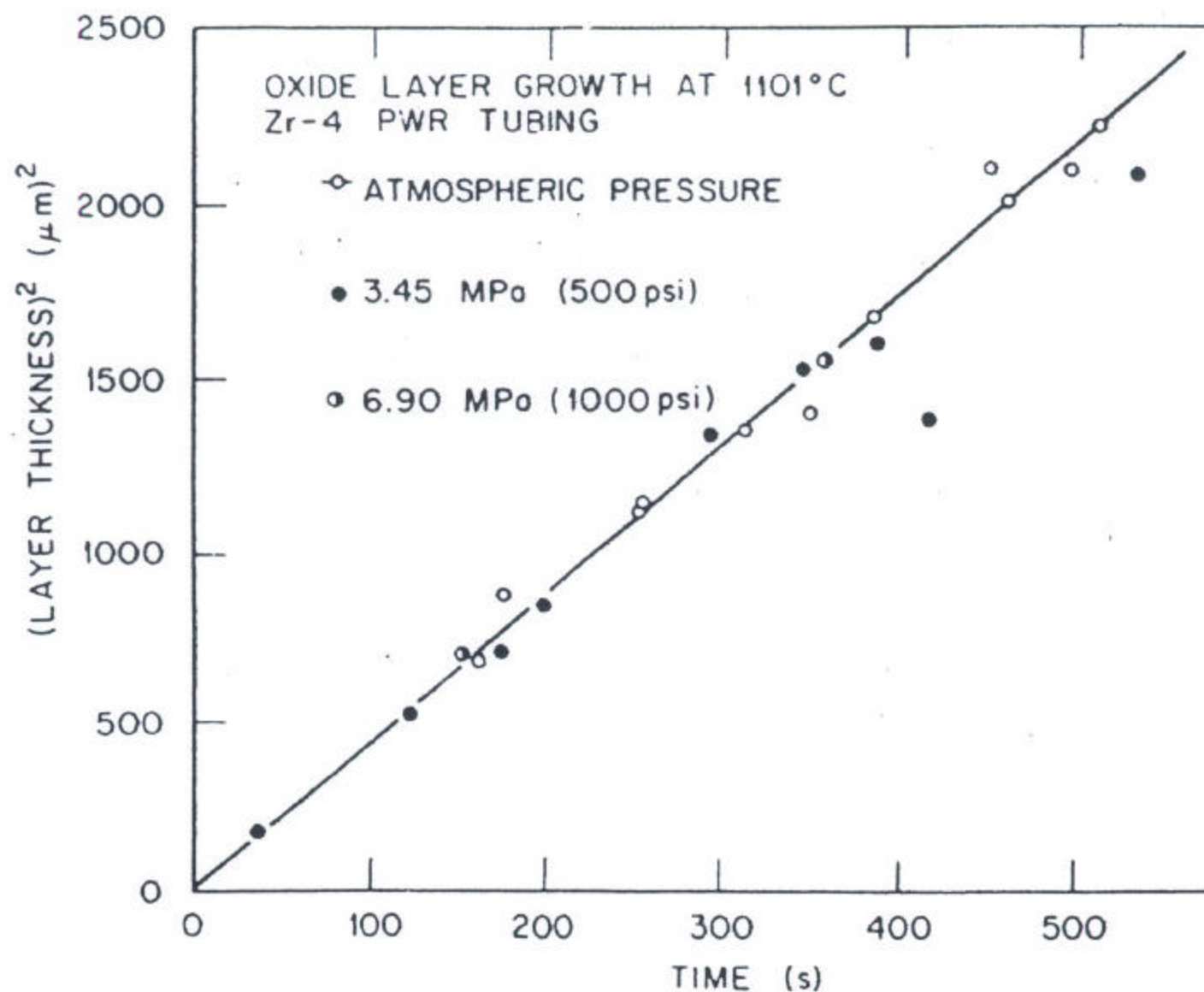


Fig. 4. Oxide layer growth during oxidation of Sandvik zircaloy-4 PWR tubing at 1101°C in steam at 3.45 MPa (500 psi), and at atmospheric pressure. Solid line represents data for oxidation at atmospheric pressure.

ZRY-4 / HIGH PRESSURE STEAM

- Pawel and Park associate their observations with the tetragonal/monoclinic transition of ZrO_2 :
- Below $\sim 1100^\circ\text{C}$, the tetragonal phase is initially stabilized by the coupled effects of:
 - Compressive stresses at the metal/oxide interface (high Pilling-Bedworth ratio)
 - Small crystallite size
 - Substoichiometry

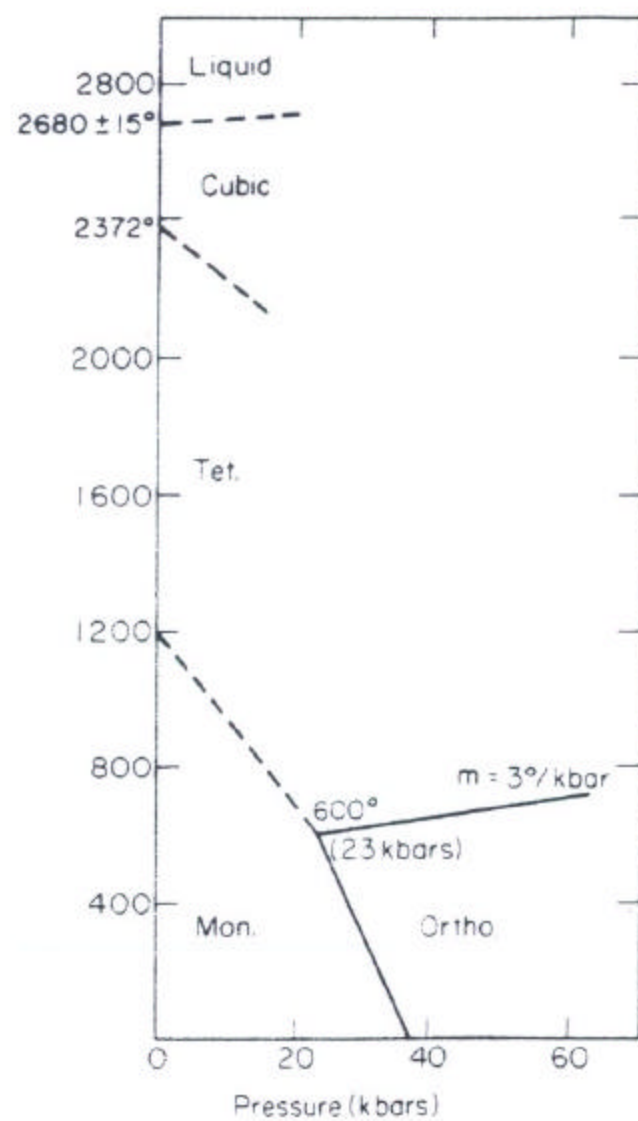


FIG. 4259.—System ZrO₂, proposed composite, as drawn by compilers after data of Refs. 2-4, 10, 11, and 17.

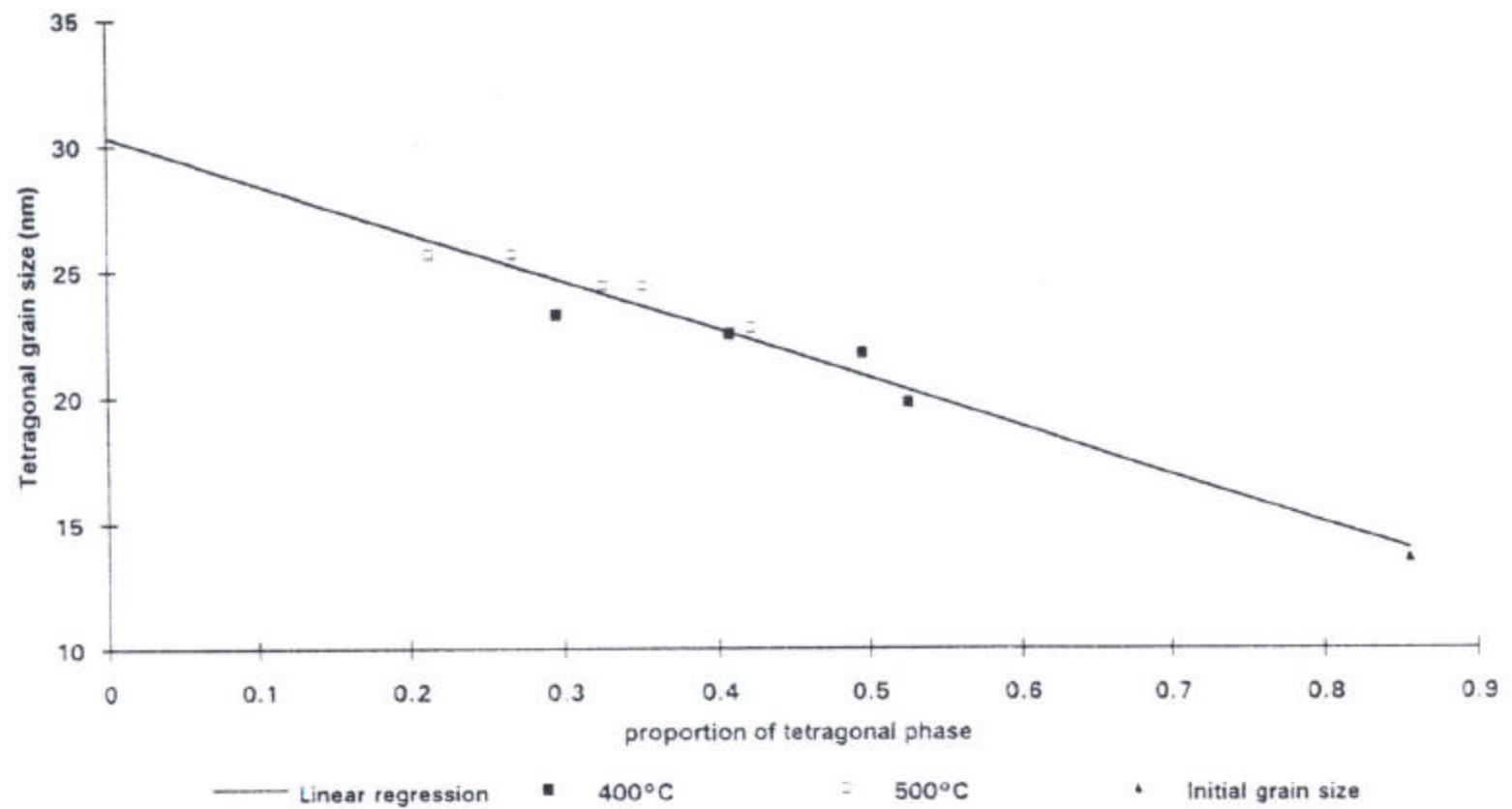


Fig. 4. Zirconia powder. Correlation between tetragonal grain size and content of tetragonal phase.

ZRY-4 / HIGH PRESSURE STEAM

- During growing, the same coupled effects induce transformation into monoclinic phase:
 - Stress relaxation
 - Crystallite growth
 - Evolution to stoichiometry
- This transformation induces microporosities and microcracks
- Model similar to Leistikow's « breakaway » model at $P_{\text{atmospheric}}$ and longer times

ZRY-4 / HIGH PRESSURE STEAM

- According to Park's tests, accelerated oxidation kinetic due to steam partial pressure rather than total pressure
- Crystallite growth kinetic increases with steam partial pressure (Murase & Kato)
- High steam pressure accelerates the evolution to stoichiometry
- Park observes that temperatures at which the effect is maximal for Zry-4 (750-800°C) coincide with temperatures of Leistikow's first « breakaway » peak at $P_{\text{atmospheric}}$ and longer times

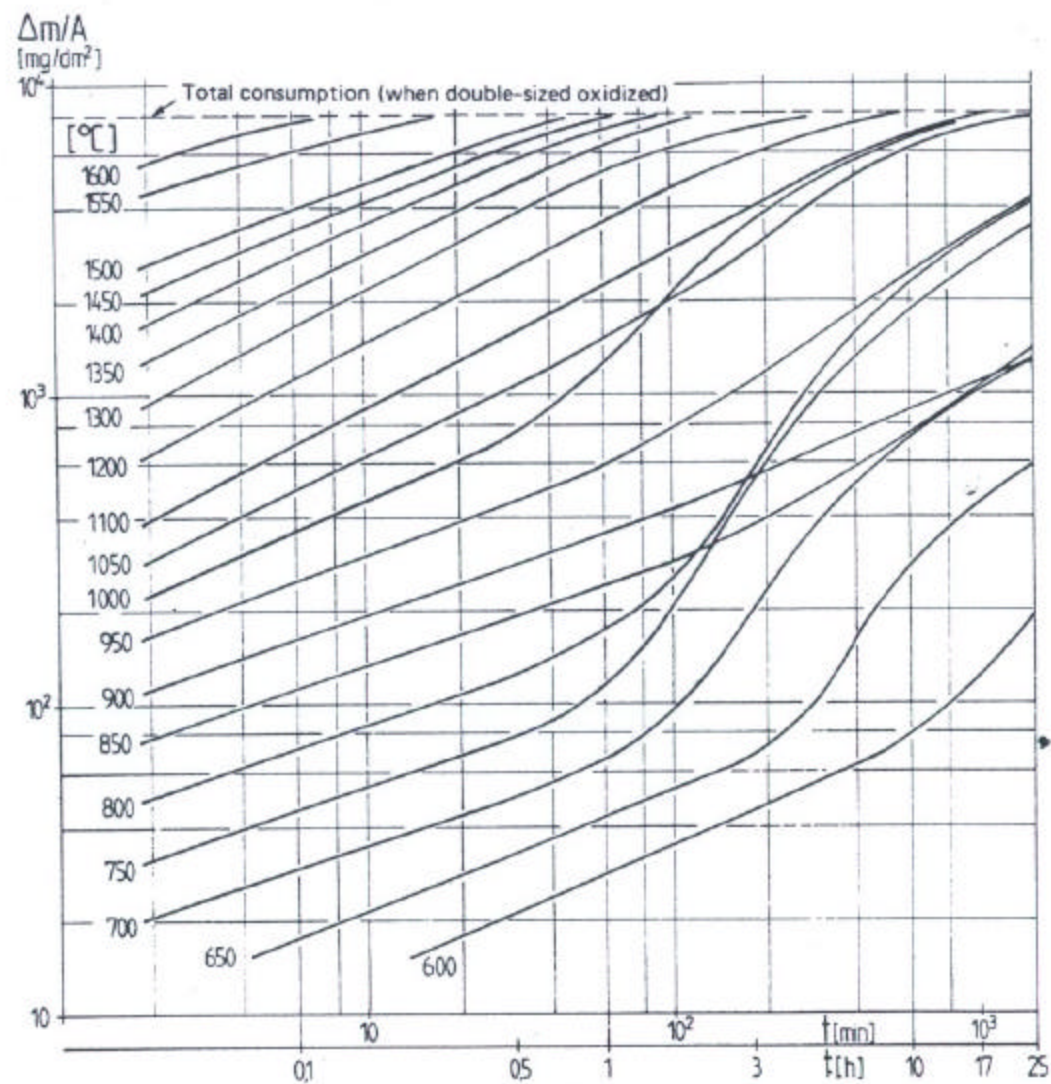


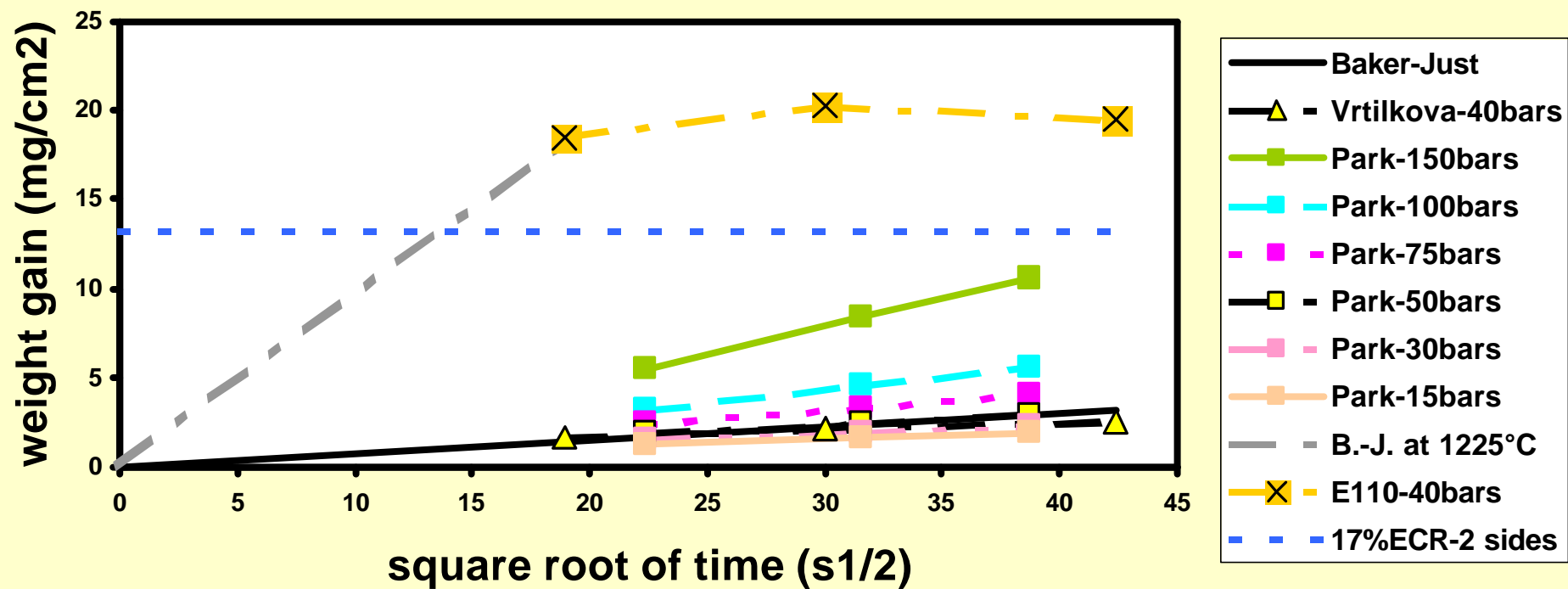
Fig. 6. Isothermal oxidation of Zircaloy-4 as function of time. Long-term exposure to high temperature steam (≤ 25 h, 600–1600°

ZRY-4 / HIGH PRESSURE STEAM

Conclusion for fresh Zry-4:

- In the 25-50bars range, the kinetik is enhanced (>Baker-Just), but limited in absolute value (relative maximal effect at 750-800°C)
- No actual safety problem for intermediate break LOCA with FRESH Zry-4

E110 / Zry - weight gain at 850°C as a function of square root of time and steam pressure



1%Nb ALLOYS / H. P. STEAM

- At 750°C, pressure effect lower than for Zry-4
- At 850°C and 40bars, strongly enhanced initial kinetic for E-110 alloy (>17% ECR-2 sides, even without wall thinning by ballooning) (Vrtilkova)
- temperatures of « breakaway » peak at $P_{\text{atmospheric}}$ and longer times (>835°C) coincide with temperatures at which the pressure effect is maximal for E-110
- Lack of data for new Nb-containing western alloys, need of tests

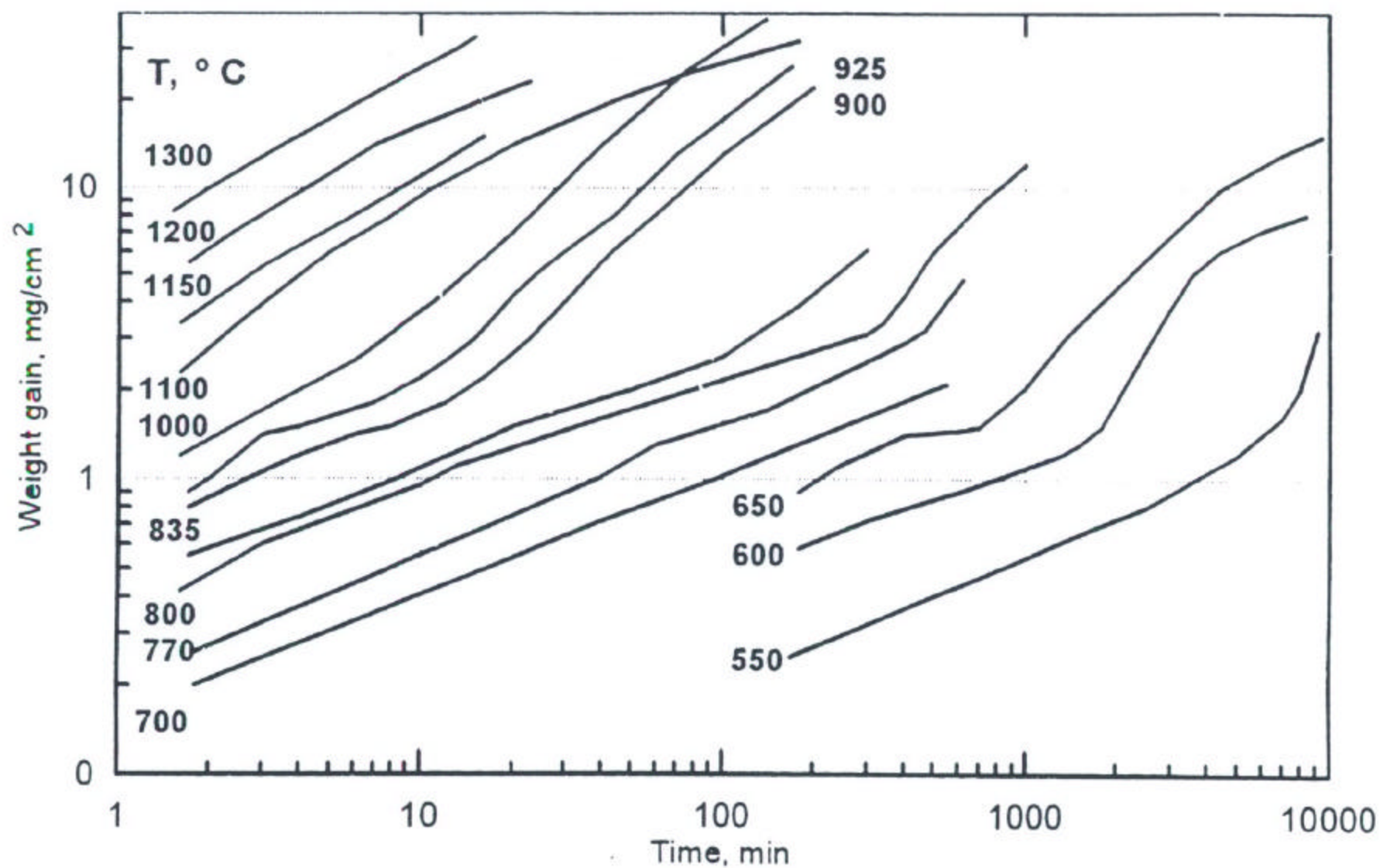


Fig. 2 Weight gains of VVER-type claddings oxidized in steam at atmospheric pressure

H. BURNUP ZRY-4 / H. P. STEAM

- Lack of data for high burnup (hydrided) Zry-4
- Known role of hydrogen on the tetragonal to monoclinic transition (JAERI)
- Need of tests

H. P. STEAM / CONCLUSION(1)

- As post-quench ductility and long term « breakaway » at $P_{\text{atmospheric}}$, but unlike short term weight gain kinetic at $P_{\text{atmospheric}}$, H.P. steam oxidation behavior cannot be extrapolated from one Zr alloy to another one
- Fresh Zry-4: no actual safety problem for intermediate break LOCA

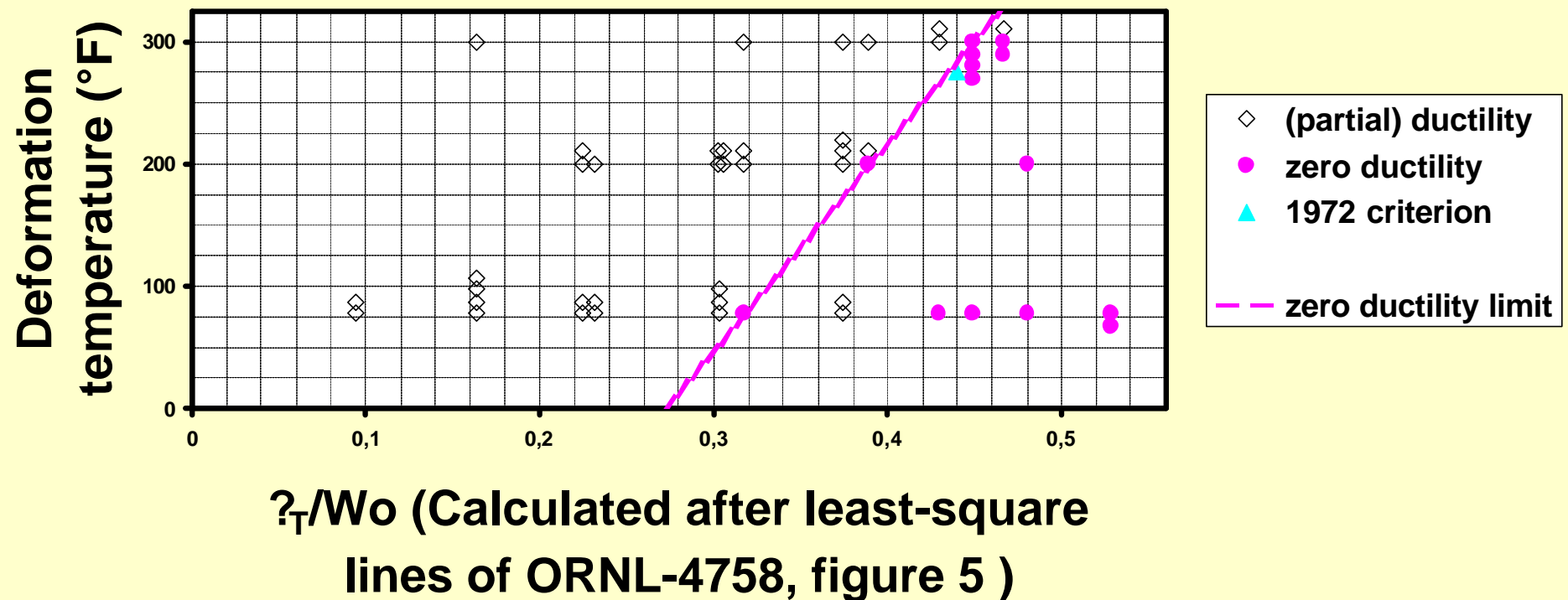
H. P. STEAM / CONCLUSION(2)

- E-110 alloy: strongly enhanced initial kinetic at 850°C and 40bars
- Nb-containing western alloys and high burnup Zry-4: lack of data, need of tests
- First tests under preparation in France (EdF-Framatome-CEA) to start in 2003

17% ECR and Baker-Just

- First step of the criterion: Zero ductility temperature (ZDT) < 275°F (135°C)
- Second step based on Hobson's slow-ring-compression tests: $\delta_T/W_O < 0.44$
 - δ_T : combined thickness of oxide and α -Zr(O) layers
 - W_O : thickness before oxidation

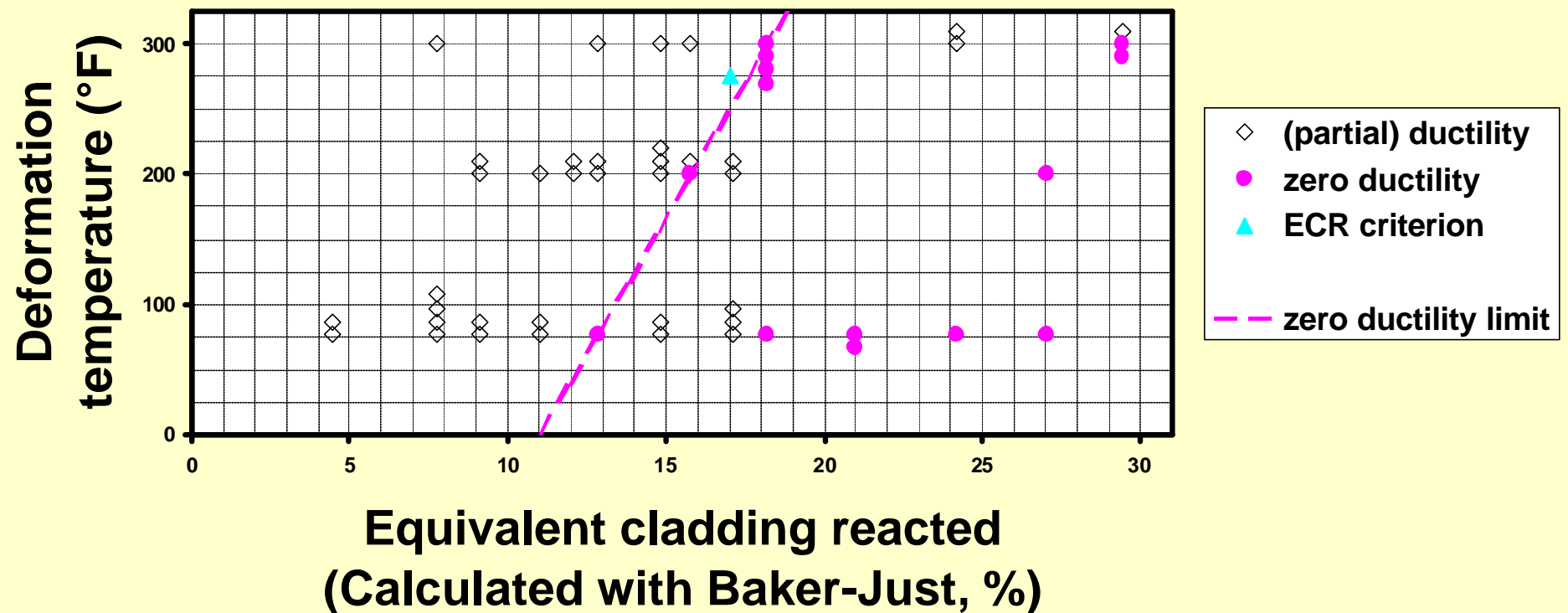
Hobson's slow ring-compression tests - Specimen ductility as a function of deformation temperature and $\dot{\epsilon}_T/W_o$ (Calculated after ORNL-4758, figure 5)



17% ECR and Baker-Just

- Same calculational procedure as in the Hearing Concluding Statement
- When specimens had same time at oxidation temperature and same compression temperature, artificial displacement by 10°F, upwards for the (partially) ductile ones and downwards for the zero ductility ones
- Very good straight limiting line crossing 275°F at ~0.44

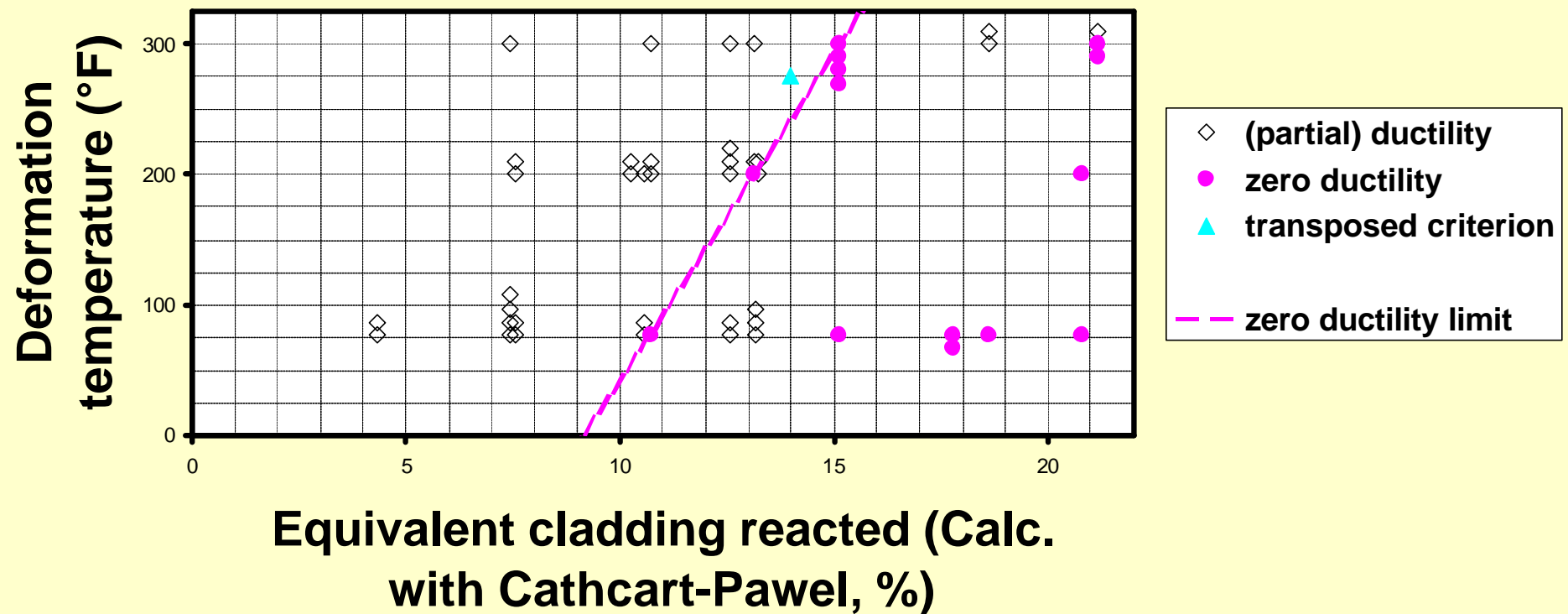
Hobson's slow ring-compression tests - Specimen ductility as a function of deformation temperature and ECR (Calculated with Baker-Just)



17% ECR and Baker-Just

- Third step based on a calculation with the Baker-Just correlation: $ECR < 17\%$
- Again, very good straight limiting line crossing 275°F between 17 and 18%
- 17% chosen as rounded value at the left
- Now hypothetical fourth step based on the Cathcart-Pawel correlation

Hobson's slow ring-compression tests - Specimen ductility as a function of deformation temperature and ECR (Calculated with Cathcart-Pawel)



17% ECR and Baker-Just

- Again, very good straight limiting line crossing 275°F between 14 and 15%
- 14% would have been chosen as rounded value at the left, if the Regulatory Staff would have had and used in 1973 the Cathcart-Pawel correlation
- Baker-Just correlation must be used for comparison with 17%, but not necessarily for calculation of chemical heat

CATHCART-PAWEL

- Weight gain correlation used in RG 1.157 and recommended in Research Information Letter (RIL) 0202
- Weight gain measured by the metallurgical method (assumed stoichiometric oxide)
- Surprise in appendix B of ORNL/NUREG-17: high hydrogen uptake (up to 1096wtppm)
- Explanation: steam leaks at the inner side (oxidation nominally only at the outer side)

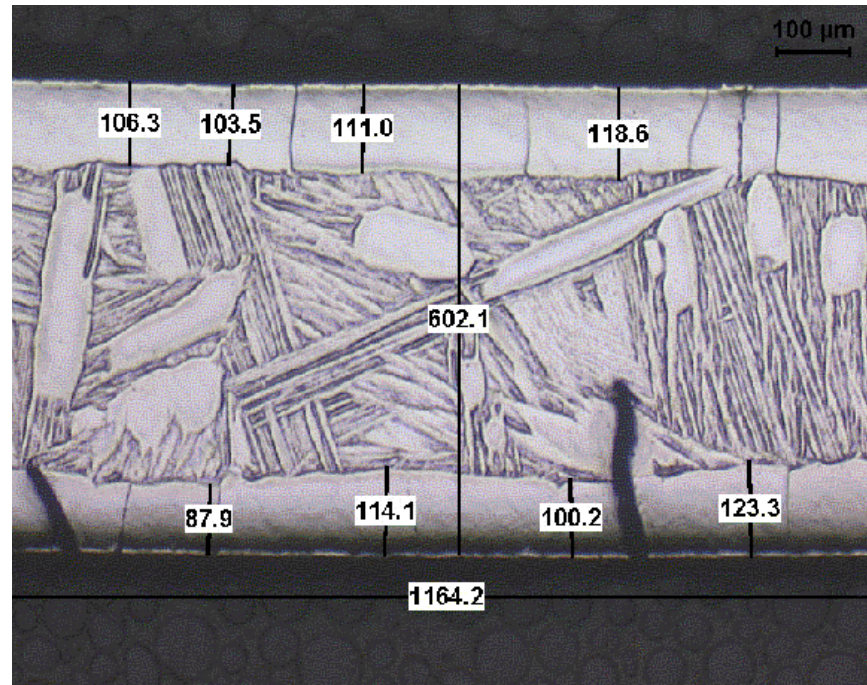
CATHCART-PAWEL

- Cathcart and Pawel were ignoring the hydrogen effect on the Zr(H)-O diagram
- Now we know that H stabilizes β Zr, increasing the O solubility, and destabilizes α Zr(O), a greater O content being necessary to stabilize α Zr(O) in presence of H
- Confirmed by recent tests in France, sponsored by IRSN and EdF

Zy-4
+ 0.5 wt% O₂
without H₂

(optical micrographs
obtained after
annealing for 3
hours at 1100°C)

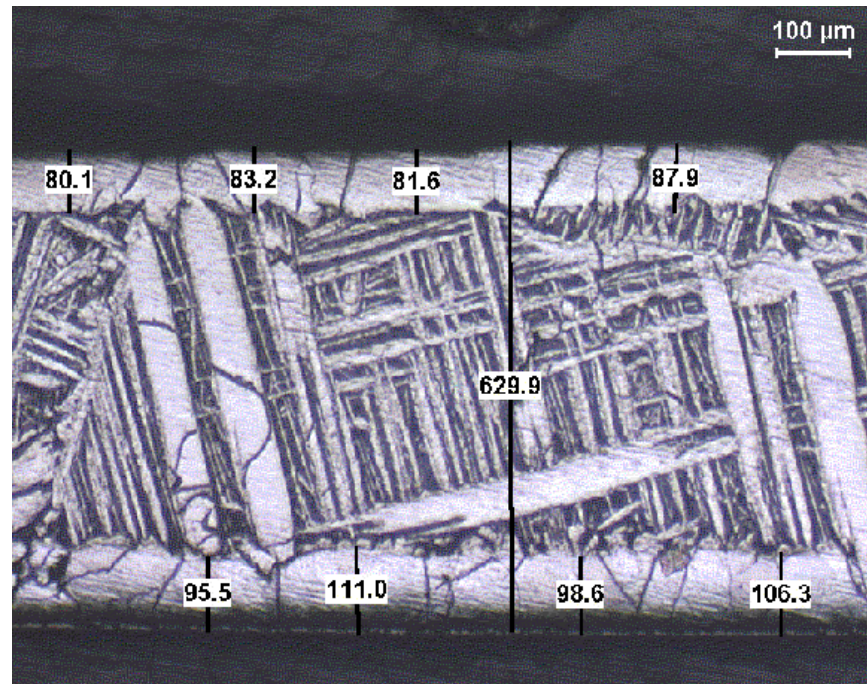
Zy-4
+ 0.5 wt% O₂
+ 1000ppm H₂



← *a-phase layer*

↑ *Ex-b*
 ↓ *phase*

← *a-phase layer*



← *a-phase layer*

↑ *Ex-b*
 ↓ *phase*

← *a-phase layer*

CATHCART-PAWEL

- One specimen H precharged
- Both O charged at a given % by 2-side oxidation
- Annealing to dissolve the oxide layers up to the thermodynamic equilibrium
- H reduces $\alpha\text{Zr(O)}$ thickness and increases βZr thickness

CATHCART-PAWEL

In the metallurgical measure of the weight gain by Cathcart and Pawel:

- O concentrations in the βZr and $\alpha\text{Zr(O)}$ phases are underestimated, $\alpha\text{Zr(O)}$ thickness is reduced
- This is compensated for by the oxide stoichiometry assumption
- Cathcart-Pawel correlation coincides with Kawasaki's one (2-side oxidation, no H uptake, weighing)

CATHCART-PAWEL

- Cathcart-Pawel correlations cannot be used for the calculation of β (Hobson), relative (Scatena, Sawatzky) or absolute (Chung & Kassner) β thickness
- As Cathcart-Pawel weight gain correlation coincides with Kawasaki's one, it may be used for the calculation of chemical heat, provided that the uncertainties are taken into account (in a RG 1.157 approach, not in an Appendix K approach)